The MIT Marine Industry Collegium
Opportunity Brief #20

# Protection of Materials in the Marine Environment

A Project of
The Sea Grant College Program
Massachusetts Institute of Technology
MITSG 80-7

The MIT Marine Industry Collegium

# PROTECTION OF MATERIALS IN THE MARINE ENVIRONMENT

Opportunity Brief #20

Revised Edition

July 7, 1980

Marine Industry Advisory Services

MIT Sea Grant Program

Cambridge, Massachusetts 02139

Report No. 80-7

Index No. 80-707-Kni

## PREFACE

This Opportunity Brief and the accompanying Workshop (held on April 11, 1980) were presented as a part of the MIT/Marine Industry Collegium program, which is supported by the NOAA Office of Sea Grant, by MIT and by the more than 110 corporations and government agencies who are members of the Collegium. The underlying studies were carried out under the leadership of the Principal Investigators named in the report, but the author remains responsible for the assertions and conclusions presented herein.

Through Opportunity Briefs, Workshops, Symposia, and other interactions the Collegium provides a means for technology transfer among academia, industry and government for mutual profit. For more information, contact the Marine Industry Advisory Services, MIT Sea Grant, at 617/253-4434.

Norman Doelling

July 7, 1980

TABLE OF CONTENTS

## 1.0 Overview

This Opportunity Brief and the associated Workshop represent a collaborative effort of the Sea Grant Programs of the Massachusetts Institute of Technology and Louisiana State University. The Workshop was held at Baton Rouge on 11 April, 1980. Its objectives were to introduce Collegium members to LSU engineering resources and activities in marine studies and technology, and to provide progress reports on some current research programs at LSU.

The morning session focused on two emerging technologies: remote sensing of the ocean environment via satellites, and computer-aided mechanical and structural design. Computer analysis of satellite image data could be of importance to general oceanographic and ocean engineering studies. Computer-aided design will have an increasing impact on naval architecture and the design and construction of offshore structures. Demonstrations at the Workshop provided attendees with a preview of new tools that will become available in the years ahead.

In the afternoon the emphasis was on the degradation and protection of materials in the marine environment, a central theme of Sea Grant research at LSU. A major effort at LSU is the understanding, modeling, and design of antifouling coatings for ships, offshore structures, and pilings. The costs of fouling on hulls can be measured in terms of increased fuel usage due to drag, the expenses of dry docking for scraping and coating, and the environmental impact of some of the traditional antifoulants (mercury, arsenic, and lead). Fouling on offshore structures is of particular interest since it increases the wave induced forces on the structure and creates problems in the inspection of the structure for damage.

Research reported on hydrogen embrittlement of metals in the marine environment, particularly in the presence of cathodic protection systems.

Another presentation described some findings in corrosion/erosion resistance coatings for steel, including plasma-sprayed TiN-Aluminum and $TiO_2$-Al coatings.

Abstracts of the Workshop presentations are presented in the following sections.

## 2.0 Two Emerging Technologies for Marine Engineering

### 2.1 Remote Sensing - TIROS Satellite Data

Using TIROS Satellite data, which are calibrated to temperature, Professor Charles Harlow of LSU is developing techniques for the computerized detection and verification of water mass boundaries, such as shorelines. With this system, water patterns in the entire Gulf of Mexico can be monitored and studied as if one were looking at a small lake. Concentration of atmospheric parameters, such as haze and humidity, can also be established for the entire Gulf region.

In addition to having obvious applications in the mapping of coastal areas, this system could have broad uses in gathering engineering data for design of offshore structures, weather forecasting, and fisheries management, for example, in the correlation of water temperatures and fish populations. Military applications are also possible in connection with underwater detection and surveillance. Recent research has focussed on the daily monitoring of floods along the Mississippi River.

The system and its ability to display various coastal phenomena was demonstrated at the Collegium Meeting.

Professor Harlow also discussed his research on the computerized analysis of imagery. The basic goal of this work is to develop algorithms that model human perception of images. He is specifically concerned with texture analysis algorithms. The work covers evaluation of existing texture analysis algorithms, determination of measures that accurately represent features used by humans in discriminating texture patterns, and the development of improved methods for analyzing texture in images.

## 2.2 Computer Aided Design: Towards a Natural Interactive Design Environment

In the years to come, designers of ships and offshore structures will have increasing access to computer-aided design tools. The effectiveness of these new tools will depend largely on the extent to which digital machines can be made to accept and work with the forms of input most natural to designers, including free hand sketches and conversational language, both written and spoken. Professors Brewer, Thompson, and McPhate of LSU described their research as it relates to the creation of a design environment in which the computer becomes a natural extention of the designers mind. The emphasis is on interface tools that require little or no training on the part of the designer and that result in a high level of control over the design process.

Recent research efforts contributing to the achievement of a proper design environment were reviewed, and some of the problems remaining to be solved will be presented. LSU's activities in man-machine communication for a design environment have involved computer recognition of two and three dimensional, free-hand sketches, design of interactive input devices, digital controls, voice communication, natural language processing, interpretive systems, mathematical modeling, optimization, geometry-based data structures, and interactive data management.

## 3.0 Materials in the Marine Environment

### 3.1 Antifouling Marine Coatings - Effectiveness and Safety of Organotin Containing Materials

#### 3.1.1 Background and Motivations

Underwater or splash zone marine structures are subjected to a very harsh environment where corrosion and biofouling combine to cause millions of dollars annually in maintenance costs. An extensive critical report by the Naval Ship Engineering Center in 1977 (1) concluded that the US Navy alone lost more than $215 million in 1974 due to fouling-related deterioration of wood docks and piers and fouling growth on ships' hulls. The report further points out that although new noncoating antifouling systems and electrical anticorrosion systems are functioning, the state-of-the-art in marine facility protection is a coating system; generally a two-component systems consisting of an anticorrosive coating covered by an antifouling coating.

The critical need to provide corrosion protection has biased research and development towards anticorrosion procedures, with less emphasis being placed on the development of long lasting antifouling coatings. Effective service lifetimes of six or seven years are common for anticorrosion coatings, but the maximum service life of antifouling coatings is three years or less. This disparity is of particular concern since the failure of an antifoulant coating subjects the anticorrosion coating to intrusions from the bioorganisms, with subsequent failure practically guaranteed. In addition, microorganisms colonizing on a metal substrate may provide an environment where corrosion is actually enhanced (2-7).

The design of new, longer lived antifouling coatings and anticorrosion/antifouling coating systems which are environmentally compatible is a very high priority for the marine industry. Professor Mary Good of LSU has developed methods for the detailed characterization of successful antifouling coatings and the determination of their environmental impact. This work provides the necessary background to develop laboratory criteria for successful antifouling coatings and to complete studies on the final environmental fate of the toxicants released from the potentially successful organotin containing antifouling coatings. Using specialized equipment and spectroscopic techniques, Professor Good has begun a study of the corrosion process that takes place in the presence of bioorganisms.

### 3.1.2 Objectives

Specific objectives for the continuation of Professor Good's program are:

1) The completion of the modeling work required to reduce earlier experiments with toxicant leaching to a working laboratory evaluation procedure for new antifouling coatings and/or formulations;

2) the completion of speciation work on the released organotin toxicants and an evaluation of their long term environmental fate; and

3) the implementation of a new program aimed at understanding the corrosion mechanism associated with microorganism colonization on metal surfaces and the corrosion processes associated with marine organism intrusion of protective marine coatings.

### 3.2 The Effect of Hydrogen Concentration and Impurity Elements on the Hydrogen Embrittlement of Iron

Metal structures exposed to marine or coastal environments can experience time-dependent deterioration of their mechanical properties. Corrosion and hydrogen embrittlement are two mechanisms by which the mechanical properties of a system can be detrimentally reduced. Steel structures can be very susceptible to hydrogen embrittlement, particularly in marine environments where hydrogen is present due to corrosion processes and cathodic protection systems.

The embrittlement of steels by hydrogen may manifest itself as a loss of ductility and it may significantly reduce the load carrying capacity by decreasing the stress necessary for fracture or crack propagation. Other artifacts that may result from the adsorption of hydrogen are blistering and the formation of cracks or voids within the structure, without stresses being applied. The degree to which a steel is embrittled is a function of its strength level, high strength steels being more susceptible to brittle fracture or stress assisted cracking.

Cathodic protection systems are an important tool in the prevention of corrosion of coastal and offshore structures. However, cathodic protection increases the likelihood that hydrogen will be present in the environment surrounding the protected structure, thus increasing the probability of structural failure at load levels below that for which the structure was designed. As the use of high strength steels becomes more common in offshore structures, it becomes increasingly important to understand the phenomenon of hydrogen embrittlement. There is a need to determine the mechanism by which hydrogen embrittlement occurs, to study how the degree of embrittlement is affected by alloying elements and the environment, and to collect data that can be used by the engineer in the selection of materials for use in marine structures.

Professor Shelton of LSU is currently studying the embrittlement of pure iron (and iron with a small amount of impurity elements added) as a function of stress level at the crack tip and composition. The proposed experimental outline calls for the study of the effect of impurities and deformation on the hydrogen trapping characteristics and the development of hydrogen rich centers within the iron using permeation and TEM studies.

### 3.3 Protection of Metals in Marine Services by the Use of Metallic Coatings

Professor Raman of LSU presented a brief survey of the metallic coatings in common use in marine sciences, methods commonly used in coating steels, and adequacies and deficiencies of some of the coatings. He also discussed the need for development of more efficient coatings and presented results of a study at LSU on titanium-based coatings, with a brief analysis of the properties and projected benefits of titanium. Corrosion characteristics of several plasma sprayed TiN-Al and TiO2-Al composite coatings on steels in salt water were discussed.

Coatings can be developed with or without other suitable undercoatings and they can also be protected by suitable topcoats. Results indicate that the addition of TiN and, possibly, other such compounds to aluminum coatings on steels would be beneficial in improving their erosion/corrosion resistance. A coating of TiN does corrode in salt water, but adding aluminum to it improves corrosion resistance. Coatings with compositions containing 75 or 90 wt.% Al and the rest TiN have been found to possess combinations of good corrosion and wear resistances in salt water. These coatings do not show any pitting and also protect steel sacrificially. They are expected to be good at somewhat elevated temperatures and in harsh environments of geothermally heated saline waters.

A pure titanium coating being developed in Japan and the USSR would be cathodic to steel, but could still possess enough ductility, toughness and freedom from defects to be valuable in practice. Studies at LSU indicate the feasibility of developing a titanium-based alloy composition that would be anodic and sacrificial to steel.